Heavy Hydrogen and Heavy Water

IN a lecture delivered before the New York Section of the American Chemical Society on December 8, Prof. H. C. Urey gave some further information as to the properties of the heavy hydrogen isotope of mass 2.01356, that of light hydrogen being 1.00778 (both on the $O^{16} = 16$ scale).

Attempts had been made to separate the hydrogen by fractional distillation of the liquid, calculation showing that the vapour pressures should be different, but the method was not successful because the low surface tension of liquid hydrogen makes it difficult to prevent its escape as mist in the fractionating column. A method depending on diffusion into flowing mercury vapour was no more effective. Some details of the actual method of separation, depending on electrolysis with water-cooled nickel electrodes in cells each containing 300 c.c. of potash solution in water from commercial cells enriched to 0.5-1 per cent of "deuterium oxide", are given. The current is 25 amp., and 30 cells are placed in series across 110 volts. Electrolysis is carried on until the volume is reduced to one third, when the residual electrolyte is removed, two thirds distilled from the potash, and combined with the undistilled liquid. Electrolysis to one third is again carried out, and beginning with the second stage, the hydrogen and oxygen gases are recombined to give a liquid containing 0.3-0.4 per cent of "deuterium The progress of the fractionation is oxide". followed by observation of the refractive index.

Investigations on the equilibrium

$2\mathrm{H}^{2}\mathrm{I} \rightleftharpoons \mathrm{H}_{2}^{2} + \mathrm{I}_{2}$

gave results agreeing with calculations which show, for example, that the ratio of the equilibrium constants with light and heavy hydrogen should be 1.222 at 700° abs. The equilibrium constants for the reaction

$H_{2}^{1} + H_{2}^{2} \equiv 2H^{1}H^{2}$

gave 3.28 (3.27), 3.73 (3.77) and 3.75 (3.82) at 298.1°, 671° and 741°, abs., the calculated values being in brackets¹. Experiments by Crist and Dalin showed that no interaction between heavy hydrogen and the light hydrogen of water over which the gas was confined had occurred in a few weeks; the different result reported by Oliphant² may have been due to the presence of a catalyst.

Experiments by Rittenberg and Urey on the electrolytic separation of hydrogen isotopes pointed to a kinetic explanation of the phenomenon; unless the differences in electrode potentials are much greater than those indicated by calculations, it does not seem possible that the separation is due to this cause³. The physiological properties of heavy water are supposed to depend on possible differences in ionisation constant and in reaction velocities as compared with ordinary water. A design of electrolytic cell for concentrating heavy water has been described by Harkins and Doede⁴ but no details of performance are given. The specific rates of discharge of light and heavy hydrogen atoms on various metal cathodes have been measured by Topley and Eyring⁵ and the results considered with reference to the theory of over-voltage : they are not inconsistent with the view that the separation is almost entirely due to the zero-point energy difference. The slow process at the cathode does not appear to be combination of atoms to molecules.

A method for determining the concentration of the heavy oxygen isotope O^{18} in water during treatment⁶ depends on decomposing the heavy water with heated iron and combining the liberated hydrogen with ordinary oxygen from hot copper oxide and condensing the water (X) so formed. The iron oxide is then decomposed by heating in ordinary hydrogen and the water formed (Y)condensed. The water X was found to be identical with the initial heavy water, whereas Y was identical with ordinary water. Hence there is no appreciable concentration of O^{18} in the electrolytic process.

Several investigations of the properties of heavy water, in addition to those already reported in these columns', have been published. The solubilities of one or two salts in heavy water are distinctly lower than in ordinary distilled water^s: 1.000 gm. of ordinary water dissolves 0.359 gm. of sodium chloride at 25° and 1 gm. of water containing 92 per cent of hydrogen as H² dissolves 0.305 gm, a difference of 15 per cent, whilst the corresponding figures for barium chloride show a difference of 19 per cent.

The densities, refractive indices $(n_{20}^d \text{ and } n_{20}^c)$, molar refraction for D line, viscosity (η), surface tension (γ), dielectric constant (D), magnetic susceptibility (χ) and molar susceptibility of water containing 31, 63.5 and 92 per cent hydrogen as H² (assuming the density 1.1056 for pure H²₂O) have been measured, and the values extrapolated to pure H²₂O. Selwood and Frost's values⁹ are (the values for ordinary water in brackets): n_{20}^d , 1.3281 (1.3329); n_{20}^c , 1.3265 (1.3309); η_{20} , 14.2 mp (10.87 mp); γ , 67.8 (72.75); $\chi \times 10^6$ /gm. (92 per cent water), -0.65 (-0.72); molar susceptibility $\times 10^6$, -13 (-13).

Lewis and Macdonald found the viscosity at several temperatures $(5^{\circ}-35^{\circ})$ higher than that of ordinary water, but their value at 20°, 12.60, is not in agreement with Selwood and Frost's. The dielectric constant is lower than that of ordinary water : $D^2/D^1 = 0.982$ at 10°, 0.990 at 25°. The abnormality as compared with ordinary water decreases with rise in temperature for all properties investigated.

The refractive index¹⁰ affords a convenient method of determining the proportions of H_2^iO

and $H^{2}_{*}O^{10}$: the effect of the O^{18} isotope is opposite in sign from that of H², and the measurement of the density and refractivity gives the complete isotopic composition (H1, H2, O16, O18) of a sample The mutarotation of α -d-glucose in of water. heavy water shows that the displaceable hydrogen atom of the sugar is immediately replaced by H² from the water, and the mutarotation is due to a change in which the double bond in a carbonyl group, =C=0, is replaced by a ring formed by the migration of a hydrogen atom¹¹.

By the interaction of heavy water with magnesium nitride, ammonias in which the hydrogen atoms are predominatingly H² (deuteroammonias) are produced, which have higher melting points, boiling points and latent heats than ordinary ammonia12.

Further experiments on the physiological effects of heavy water¹³ show that the filaments of Spirogyra in water of specific gravity 1.000061 are characterised by lack of movement, absence of abscission or cell disjunction, and greater longevity. The usual effect with ice and steam water was confirmed¹⁴. The results suggest a stabilising action of water containing H², perhaps an effect on the colloids in the organism, the water bound in such colloids being known to be denser than free water. A slightly higher pH (as determined with bromthymol blue) for this sample of water was found. In other experiments¹⁵, decreased enzyme activity and fermentation in isotope water, a more extensive spread of Oscillatoria (perhaps due to a pH of 6.77 as determined by the glass electrode), and the following results with Spirogyra nitida were found : a representative filament of 31 cells in isotope water had 43 cells after 6 days, of which 3 were dead ; a filament of 37 cells in ordinary water showed no cell division at the end of 6 days and 20 cells died ; in ice water renewed twice daily, a filament of 50 cells showed 15 abnormal at the end of five days, whilst the filament in freshly condensed water renewed twice daily showed all its 50 cells dead or shrunken in the same period ; the control filament (pond water) had 47 cells initially and 64 normal cells after six days.

- Of Hormal Cells after Six Gays.
 ¹ Cf. A. and L. Farkas, NATURE, 132, 894, Dec. 9, 1933.
 ² NATURE, 132, 675, Oct. 28, 1933; cf. Polanyi and Horiuti, *ibid.*, 819, Nov. 25.
 ³ cf. Collie, NATURE, 132, 568, Oct. 7, 1933.
 ⁴ J. Amer. Chem. Soc., 55, 4330; 1933.
 ⁵ J. Amer. Chem. Soc., 55, 5058; 1933.
 ⁵ Selwood and Frost, J. Amer. Chem. Soc., 55, 4335; 1933.
 ⁶ Taylor, Caley and Eyring, J. Amer. Chem. Soc., 55, 4334; 1933.
 ⁸ Selwood and Frost, J. Amer. Chem. Soc., 55, 4335; 1933.
 ⁹ Taylor, Caley and Eyring, J. Amer. Chem. Soc., 55, 4334; 1933.
 ⁹ Selwood and Frost, J. Amer. Chem. Soc., 55, 5060; 1933.
 ¹⁰ Crist, Murphy and Urey, J. Amer. Chem. Soc., 55, 5060; 1933.
 ¹¹ Pascu, J. Amer. Chem. Soc., 55, 5056; 1933.
 ¹² Taylor and Jungers, J. Amer. Chem. Soc., 55, 5057; 1933.
 ¹³ Taylor and Jungers, J. Amer. Chem. Soc., 55, 5057; 1933.
 ¹⁴ NATURE, 132, 536, Oct. 7, 1933.
 ¹⁵ Barnes, J. Amer. Okem. Soc., 55, 4336; 1933.

Ernst Haeckel (1834-1914)

By PROF. E. W. MACBRIDE, F.R.S.

^{*}HE career of Prof. Ernst Heinrich Haeckel, the centenary of whose birth falls on February 16, belongs to the heroic stage of the history of the theory of evolution. In 1862, at the early age of twenty-eight, he was appointed to the chair of zoology in the University of Jena, a post which he held until his death in 1914.

Haeckel's life bears a strong resemblance to that of Huxley, for like Huxley his life's task was propaganda in favour of the theory of evolution against the then prevalent theory of the origin of species by a series of supernatural interpositions of the Divine Being. Like Huxley too, he was an ardent advocate of the animal origin of the human race. But there were marked differences between the two men; Haeckel was a harder hitter than Huxley, and withal a much more reckless one, since he was apt to make wild statements on the basis of insufficient data, as, for example, when he stated that if there were a line to be drawn between animals and men, the lower races must be included amongst the apes. The most recent anthropological studies seem to indicate that in the essential make-up of their minds the most primitive men are very like ourselves : the data and presuppositions from which they start are different and so are their customs and traditions, but granted these postulates the conclusions at which they arrive are natural enough. But on the whole, Haeckel was a sounder biologist than Huxley:

whilst he embraced with enthusiasm Darwin's arguments about natural selection, he was never deceived into thinking that the mere survival of some and the death of others could account for progressive evolution : he saw quite clearly that the vital question was the origin of the 'variations' which distinguished the survivor from his less fortunate brother, and in this matter he followed Lamarck. When he popularised his views in his famous "History of Creation" he dedicated the work to "Jean Lamarck and Charles Darwin".

Haeckel excelled Huxley also in the amount of actual zoological work which he accomplished. Thus he wrote a descriptive monograph of the Radiolaria collected by H.M.S. Challenger, giving the characters of no less than 3,600 new species. This work occupied him for ten years. He also monographed the calcareous sponges, but the greatest task which he attempted was to sketch, assuming the truth of the evolution theory, the actual course which evolution had pursued in producing modern plants and animals. His conclusions were embodied in his "Allgemeine Morphologie", of which the "History of Creation" may be regarded as a popular edition. Of course, the state of zoological and botanical knowledge at the time that these books were written was far too incomplete to permit of any but the vaguest sketches of the course of evolution, but there can be nothing but admiration for Haeckel's bold